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# CHEMISTRY OF THE ATMOSPHERE OF THE PLANET VENUS

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## Photochemistry with Bromine Lamp

Photochemical equilibrium studies using the bromine lamp which emits the 1633 A persistent line of bromine have continued with particular reference to $CO_2$. When pure $CO_2$ was irradiated dissociation could readily be observed with formation of CO and $O_2$, $O_3$ was also present and the $O_3/O_2$ ratio was comparable to that obtained with pure $O_2$. The CO: $O_2$ ratio was determined mass spectrometrically ($O_3$ decomposes to $O_2$ in the mass spectrometer), and found to be 2:1. This is in contrast to the results of some who have reported finding less than the stoichiometric amount of oxygen. The position of the dissociation equilibrium seemed to be somewhat variable, the maximum equilibrium value for $CO/CO_2$ being ~ 0.3 ($O_2/CO_2$ ~ 0.15). To try to establish the equilibrium position better, irradiations were made of mixtures of CO, $O_2$, and argon. In every case reaction to form $CO_2$ proceeded to completion. When excess CO was present, all the $O_2$ was consumed; when excess $O_2$ was present, all the CO was consumed. Close examination of the mass spectra revealed the presence of trace amounts (~0.1%) of water vapor. Experiments were then carried out in which the reaction gases were dried with extreme care. When this was done the equilibrium was shifted slightly in the direction of increased dissociation ($O_2/CO_2$ ~ 0.03) indicating that the water vapor was catalyzing the recombination reaction. The fact that no higher degree of dissociation was obtained starting with CO - $O_2$ mixtures could be explained by the purification procedures used. $CO_2$ was obtained very dry

(Coleman grade) and was further dried by low temperature distillation. CO was purified from small amounts of iron carbonyl by bubbling through sodium hydroxide solution and then drying through liquid oxygen traps. As a result of these procedures the CO, even after careful drying through a series of liquid $O_2$ traps, undoubtedly contained substantially higher amounts of water than the $CO_2$. The recombination most probably takes place via the reaction:

$$CO + OH \rightarrow CO_2 + H \qquad (1)$$

since OH radicals and H-atoms are present as photodissociation products of water. The OH radicals can be regenerated in several ways, most likely by reaction with $O_3$:

$$H + O_3 \rightarrow O_2 + OH \qquad (2)$$

As a check on the mechanism a series of irradiations was carried out on pure $CO_2$ to which traces of $H_2$ had been added. The $H_2$ molecules should react with O-atoms to form OH radicals and, if the proposed mechanism is correct, inhibit the $CO_2$ dissociation. It was found that with 0.1% $H_2$ the dissociation of $CO_2$ was completely inhibited ($O_2/CO_2 < 0.005$). With 0.01% $H_2$ a small amount of dissociation occurred ($O_2/CO_2 \sim 0.02$). Thus the proposed mechanism appears to be correct. It should be noted that most of the added hydrogen remained in the form of $H_2$ as could be observed mass spectrometrically and only a small fraction was converted to $H_2O$ during the time of irradiation. Whether the dissociation maximum of $CO/CO_2 \sim 0.3$ found with pure $CO_2$ represents a trace residue of water or a true equilibrium between $CO_2$, CO, $O_2$, and $O_3$ is uncertain at this point.

These results can explain the peculiar composition of the Venus atmosphere, i.e., a high abundance of $CO_2$ with no more than a trace of either CO or $O_2$. These constituents might be expected to be present in the Venus atmosphere in relatively high concentrations due to photodissociation of $CO_2$. The most recent spectroscopic investigations from a balloon carried out by Strong and his group at Johns Hopkins seem to indicate the presence of trace amounts of atmospheric water vapor. For the above mechanism involving Reactions (1) and (2) only small amounts of water need be present. Photodissociation of the water would produce OH radicals and H-atoms which could be expected to be present in steady-state down to the cloud layer. It seems probable, therefore, that any oxygen or carbon monoxide formed in the Venus atmosphere react to regenerate carbon dioxide in the manner described above.

Irradiations of $O_2$ with traces of $H_2$ have been carried out to determine whether similar factors might be responsible for the unexpected results previously obtained for the $O_2$ - $O_3$ equilibrium. It was found that with 0.01% $H_2$ the equilibrium $O_3/O_2$ ratio was substantially reduced from 0.26 to 0.18. With 0.1% $H_2$ the ratio was reduced to 0.05. Thus it can be concluded that even more stringent controls of purity are required than had been thought in order to obtain meaningful results.

Photochemistry with Iodine Lamp

Dr. Galli has carried out a series of irradiations of acetylenic hydrocarbons using the iodine lamp and is now putting his results in a form suitable for publication. Copies of the work will be forwarded to NASA when preparation for publication has been completed.

CO + O-Atom Reaction

Studies have continued on this reaction. The work performed in the spring gave results with somewhat larger scatter than expected when the rate coefficients were calculated on the basis of a simple two body homogeneous gas phase reaction. Additional data are now being obtained including results with various third bodies such as helium. Other variables are also being considered. It is clear that such reactions as those described earlier ($CO + OH \rightarrow CO_2 + H$; $H + O_3 \rightarrow OH + O_2$) could effect the results, but no such interferences have been isolated as yet.

Microwave Emission Studies

Experiments have been carried out to determine optimum conditions for observation of microwave spectra emitted from glow discharges in $CO_2$ and $SO_2$. Several spectra have been obtained and work in this area is continuing. Evaluation of the significence of the observations is being particularly stressed.

Publications and Presentations

A paper entitled " The Bromine Lamp: Studies of the Oxygen-Ozone and Carbon Dioxide Equilibria" by B. A. Thompson, R. R. Reeves, Jr. and P. Harteck was presented at the ACS Meeting in Detroit in April 1965. This paper has been accepted for publication in " The Journal of Physical Chemistry" and is scheduled to appear in the December 1965 issue. Copies of this paper have been forwarded to NASA.

A paper entitled " Radiation Equilibria Pertinent to Planetary Atmospheres" by P. Harteck, R. R. Reeves, Jr. and B. A. Thompson was presented at the symposium on atmospheric chemistry at Visby, Sweden in August 1965.

A paper entitled " Photochemical Equilibrium Studies with $CO_2$" by R. R. Reeves, Jr. , P. Harteck and B. A. Thompson is scheduled for presentation at the ACS Meeting in Atlantic City in September, 1965 and will be submitted for publication in the next few weeks. Copies will be forwarded to NASA when completed.